Aluminium complexes of B- and N-based hydrides: Synthesis, structures and hydrogen storage properties

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**Abstract**

The storage of hydrogen in a solid state is one of the main challenges for stationary and mobile applications. Light metal hydrides have attracted significant attention as potential candidates for energy storage. Remarkably, Al-containing hydrides, namely AlH₃ and M(AlH₄)ₓ, are among the most fascinating classes of materials, able to cycle up to 5.5 wt% of hydrogen at moderate temperatures. This review covers the recent research on the families of Al-based complex hydrides involving other light elements such as B and N. They were classified according to the charge of the Al-based complexes, as anionic, molecular, cationic or “autoionized” where Al is centering both the cation and the anion. The factors influencing the stability and the hydrogen purity of the series of anionic aluminium amides M[Al(NH₂)₄]ₓ, borohydrides M[Al(BH₄)₄] and amidoboranes M[Al(NH₂BH₃)₄], as well as molecular [Al(L)(BH₄)₃] (L = molecular ligands) and cation [Al(NH₃)₆]³⁺-based complexes are discussed. In particular, the ability of the strong Lewis acid Al³⁺ to coordinate both the initial hydrogenated species as well as their dehydrogenation products makes it a good template for chemical transformations involving light chemical and complex hydrides.

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**Introduction**

An increase in the consumption of non-renewable fossil fuels is producing not only a challenge of new sustainable energy carriers, but also leads to environmental pollution and climate changes induced by carbon dioxide CO₂. Thus the transition towards a new carbon-free and reliable energy system capable of substituting current and future energy demands is one of the greatest challenges of the 21st century. In line with these demands, hydrogen has an extreme potential as the cleanest energy carrier, see e.g. Ref. [1]. It can be produced from renewable energy sources by electrolytic water splitting from hybrid solar–hydrogen or other systems [2]. However, a major challenge in the future of the “hydrogen economy” is the development of efficient hydrogen storage systems, especially for mobile applications [3,4]. In particular, the efficient storage of pressurized and liquefied hydrogen has technical issues of high pressures (350–700 bar) and cryogenic temperatures (−253 °C) [4]. That is why in recent years much attention was paid to solid state hydrogen storage in a form of light metal complex and chemical hydrides, from which hydrogen can be released either by thermolysis or via hydrolysis [5–8].
Mobile applications is one of the most important directions for the “hydrogen economy”. According to the U.S. Department of energy, perspective systems for mobile applications require high hydrogen content which should be above 5.5 wt %, and a low gravimetric density of 40 g/L [9]. The second important detail is a low operational temperature (60–120 °C), suitable for proton-exchange membrane fuel cells PEMFC [10]. These requirements, together with reversibility, are limiting the number of possible solid state hydrogen storage systems. It is noteworthy that nowadays most of the advanced systems in terms of these limitations should contain light atoms (approximately with atomic number Z ≤ 13). That is why Al-containing hydrides of AlH₃ [11,12] and alkali metal alanates [13], which potentially contain up to 10.1 wt% of hydrogen and a metal which is highly abundant in nature, has attracted a great deal of attention. NaAlH₄ is the most intensively studied member of Al-based hydrides due to its high hydrogen capacity of 5.6 wt% and hydrogen release reversibility, when catalyzed by a small amount of a transition metal catalyst (e.g. 2–4 mol% Ti) [14–16]. This fascinating discovery was a breakthrough in solid state hydrogen storage systems in terms of these limitations which potentially contain up to 10.1 wt% of hydrogen and a metal which is highly abundant in nature.

Since that time, the systems of AlH₃ and M[AlH₄] (e.g. 13], which potentially contain up to 10.1 wt% of hydrogen and a metal which is highly abundant in nature, has attracted a great deal of attention. NaAlH₄ is the most intensively studied member of Al-based hydrides due to its high hydrogen capacity of 5.6 wt% and hydrogen release reversibility, when catalyzed by a small amount of a transition metal catalyst (e.g. 2–4 mol% Ti) [14–16]. This fascinating discovery was a breakthrough in solid state hydrogen storage systems since it exhibits approximately twice the reversible capacity of any of the conventional metal hydrides (e.g. LiNi₃H₆, FeTi₂H₆) [17]. Since that time, the systems of AlH₃ and M[AlH₄] have been intensively investigated both in terms of their crystal structures [18] and hydrogen storage properties [13].

The interest in Al-containing complex hydrides and their reactive hydride composites (RHC) as perspective hydrogen storage systems remained high during last two decades. Indeed, in recent years, many new Al-based complex hydrides involving other light elements such as N and B have been characterized. In particular, the synthesis, crystal structures, thermal decomposition and hydrogen storage properties of hydridic M[Al(NH₃)₄]ₙ, (M = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, n = 1; M = Ca²⁺, Mg²⁺, Sr²⁺, Ba²⁺) [19,20] and M[Al(BH₄)₄] (M = Li⁺, Na⁺, K⁺, NH₄⁺, Rb⁺, Cs⁺) have been described recently [21,22]. The other direction of perspective B,N-containing systems is making use of N—H⁺⋯—H—B dihydrogen bonds, which play an important role in molecular packing in crystals and H₂ evolution [23]. In line with this criteria, several Al-based B- and N-containing hydrides, such as an anionic Na[Al(NH₂BH₃)₄] [24], molecular [Al(NH₃)₄]BH₄ holds 25] and cation [Al(NH₃)₆]⁺ derivatives, namely [Al(NH₃)₄]BH₄ (26], [Al(NH₂)₆]Li₂[BH₄] and [Al(NH₂)₆]Li₂[BH₄] have been described [27,28].

This review paper will give a short description of synthesis, crystal structure and hydrogen storage properties of aluminium complexes with B- and N-based hydrides. We will not cover the systems where only hydrogen atoms are surrounding the central Al atom, such as alanates and in alanate, referring the reader to the existing recent reviews [11–13]. Here we focus on those compounds where Al³⁺ cation is coordinating to complex hydrides created by other light elements such as B and N. Borohydrides M[BH₄]ₙ, amides M(NH₂)ₙ, and amidoboranes M(NH₂BH₃)ₙ, themselves carry a significant amount of hydrogen, but their chemistry with alkali and alkali-earth metals is limited by the choice of metals [29–31]. Introducing another complex-forming elements allows tuning stability of bimetallic series, as illustrated for example by Zn- and Cd-based borohydrides [32,33]. Importantly, the complex-forming metal, possessing higher electronegativity, is determining the stability of the bimetallic hydride [34]. Aluminium stands in the bimetallic series on its own, given its high polarizing power defined by the exceptional charge-to-radius ratio, low weight, high natural abundance, and the fact that the chemistry of Al complexes with B- and N-based hydrides has been explored only recently. Being an excellent Lewis acid, Al³⁺ is capable of coordinating the initial B- and N-based complex hydrides and their dehydrogenation products, thus serving as a template (or a matrix) for potential reversible dehydrogenation. The activation of neutral molecules, namely ammonia and ammonia borane, also requires a highly polarizing cation and have attracted increasing interest [7].

The systems listed above will be divided into three main groups. The first contains Al-centered complex anions, namely M[Al(NH₃)₄]ₙ, M[Al(BH₄)₄] and M[Al(NH₂BH₃)₄]. The second are the molecular complexes and the third are complexes containing Al within complex cations, as for example [Al(NH₃)₆]³⁻. There are also recent examples of “autoionized” complexes, where Al forms complex cation and anion within the same compound. The presence of dihydrogen bonds will be considered along with the cation Al–N and Al–B complex hydrides.

### Synthesis

#### Synthesis of anionic M[Al(NH₃)₄]ₙ (M = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, n = 1; M = Ca²⁺, Mg²⁺, Sr²⁺, Ba²⁺, n = 2)

The synthesis of M[Al(NH₃)₄]ₙ can be performed in different ways, using the metals or their hydrides in presence of NH₃. Most of the alkali metal aluminium amides can be obtained by the reaction of Al in solution of the metals in liquid NH₃ [35]:

\[
M + Al + 4NH₃ \rightarrow M[Al(NH₃)₄] + 2H₂ (M = alkali metal)
\]

(1)

M[Al(NH₃)₄] can be also formed from the reaction of the corresponding MAIH₄ with NH₃ [36]:

\[
MAIH₄ + 4NH₃ \rightarrow M[Al(NH₃)₄] + 4H₂ (M = alkali metal)
\]

(2)

The formation of M[Al(NH₃)₄]ₙ (M = alkali or alkali earth metal) is also observed in the mechanochemical reaction of alkali and alkali earth metal hydrides with Al under NH₃ gas [19,20]:

\[
MH₄ + nAl + 4nNH₃ \rightarrow M[Al(NH₃)₄]ₙ + 2.5nH₂
\]

(3)

The mechanochemical treatment of their hydrides under liquid NH₃ yields M[Al(NH₃)₄]ₙ (M = alkali or alkali earth metal):

\[
MH₄ + nAlH₃ + 4NH₃ \rightarrow M[Al(NH₃)₄]ₙ + 4nH₂
\]

(4)

Ba[Al(NH₃)₄]₂ is found to be quite unstable at ambient conditions without ammonia pressure [37]. Recently, low temperature a single crystal measurement has revealed the
crystal structure of Ba[Al(NH$_3$)$_3$]$_2$: 2NH$_3$, which was synthesized in ammonothermal conditions from an intermetallic phase with Al$_3$Ba composition [38]. A similar ammoniate of Ca [Al(NH$_3$)$_3$]$_2$: NH$_3$ composition was also reported [39].

### Synthesis of anionic $M[Al(BH_4)_4]$ ($M = Li^+, Na^+$, $K^+$, $NH_4$, $Rb^+$, $Cs^+$) complexes

$Al(BH_4)_3$ has a high potential for hydrogen and energy storage, due to its high hydrogen content of 16.9 wt%. However, this is a highly pyrophoric liquid at ambient conditions, explosive in contact with air, and thus dangerous for practical applications. This feature is used in jet engines as an ignition source and has also been examined for possible application as a rocket fuel [40]. Thus, the stabilization of $Al(BH_4)_3$ in form of more stable complexes is one of the challenges for hydrogen and energy storage.

One of the first attempts to stabilize $Al(BH_4)_3$ with another alkali-metal borohydrides was performed by a reaction of MBH$_4$ and $Al(BH_4)_3$, which yields $M[Al(BH_4)_4]$ ($M = Li^+$ and $K^+$) [41,42]. Similar synthesis of the whole family of $M[Al(BH_4)_4]$ ($M = Li^+$, Na$^+$, $K^+$, $NH_4^+$, Rb$^+$, Cs$^+$) was performed recently by the interaction of $Al(BH_4)_3$ with alkali metal borohydrides [21,22,43]:

$$MBH_4 + Al(BH_4)_3 \rightarrow M[Al(BH_4)_4] (M = Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+)$$  \hspace{1cm} (5)

Remarkably, $LiBH_4$ forms two different mixed-metal borohydrides with $Al(BH_4)_3$. The second representative is $[Li_4(BH_4)]Al(BH_4)_3$, which can be obtained as the first of two stages of the reaction (5):

$$4LiBH_4 + 3Al(BH_4)_3 \rightarrow [Li_4(BH_4)]Al(BH_3)_4$$  \hspace{1cm} (6)

$$[Li_4(BH_4)]Al(BH_4)_3 + Al(BH_4)_3 \rightarrow 4Li[Al(BH_4)_4]$$  \hspace{1cm} (7)

The formation of $[Ca(BH_4)]Al(BH_4)_3$ complex was also claimed [44], but no further structural evidence of alkali-earth aluminium borohydrides formation was reported in the literature.

The mechanochemical synthesis of $M[Al(BH_4)_4]$ ($M = Li^+$, Na$^+$, $K^+$) is also known [45,46]. The reported reactions between MBH$_4$ ($M = Li^+$, Na$^+$) and AlCl$_3$ revealed Cl-stabilization of $[Li_4(BH_4)]Al(BH_4)_3$ [22,24,36] and formation of Na$[Al(BH_4)_4]$Cl$_2$ solid solution having crystal structure different from Cl-free Na$[Al(BH_4)_3]$. The mixture of MBH$_4$ ($M = Li^+$, $K^+$) and AlCl$_3$ yields a mixed-metal Li$K[Al(H_4)_3]$ at room temperature [21]. This method has another serious disadvantage of so-called “dead mass” formation of MC1, which significantly reduces the hydrogen storage capacity of the system:

$$3LiBH_4 + 13AlCl_3 \rightarrow [Li_4(BH_4)]Al(BH_3)_4 + 9LiCl$$  \hspace{1cm} (8)

$$4NaBH_4 + AlCl_3 \rightarrow Na[Al(BH_3)_4Cl_2] + 3Na(BH_4)Cl_{1-x}$$  \hspace{1cm} (9)

$$9LiBH_4 + 3KBH_4 + 2AlCl_3 \rightarrow 2K[Al(BH_4)_4] + 6LiCl + LiK(BH_4)_2$$  \hspace{1cm} (10)

### Synthesis of anionic $M[Al(NH_2BH_3)_4]$ ($M = Li^+, Na^+$) complexes

The existence of $Al(NH_2BH_3)_3$ was reported by Hawthorne et al. [47], however no structural data is available for this compound to the date. Recently, attention has been paid to bimetallic derivatives $M[Al(NH_2BH_3)_4]$ ($M = Li^+$, Na$^+$), which can be obtained from the reaction of alanates and ammonia borane (AB) in THF [24,47]:

$$MAIH_4 + 4NH_3BH_3 \rightarrow M[Al(NH_2BH_3)_4] + 4H_2 (M = Li^+, Na^+)$$  \hspace{1cm} (11)

The formation of Na$[Al(NH_2BH_3)_4]$ in reaction (11) can be also made in solvent-free conditions using mechanochemical synthesis [24]. Remarkably, the reaction of LiAlH$_4$ and AB under ball-milling conditions is violent resulting in amorphous products and metallic aluminium [24,48]. The reaction of Li$_3$AlH$_6$ with AB was assumed to yield a composition Li$_3$AlH$_4$(NH$_2$BH$_3$)$_4$, however this conclusion is not yet confirmed by crystal structure data [48].

### Synthesis of molecular and cation Al$–N$ and Al$–B$ complex hydrides

The second way to stabilize $Al(BH_4)_3$ can be performed via coordination of Al to other molecular hydrides, the latter behaving as Lewis bases [49]. In contrast to $M[Al(BH_4)_4]$ ($M = Li^+$, Na$^+$, $K^+$, $NH_4^+$, Rb$^+$, Cs$^+$), where Al adopts complex $[Al(BH_4)_4]$$^{-}$ anion, the addition of molecules to $Al(BH_4)_3$ can afford Al atoms to form either molecular or cation complexes. In particular, the reaction of $Al(BH_4)_3$ with one equivalent of NH$_3$, NH$_2$BH$_3$ or CH$_3$NH$_2$BH$_3$ gives molecular complexes [22,25,50]:

$$Al(BH_4)_3 + L \rightarrow [Al(L)(BH_4)_3] (L = NH_3 or RNH_2BH_3)$$  \hspace{1cm} (12)

Interestingly, in contrast to the reaction (12), an interaction of CH$_3$NH$_2$BH$_3$ with AlCl$_3$ results in an autoionized $[Al(CH_3NH_2BH_3)_2Cl_2][AlCl_4]$ complex [22].

The complexes of $Al(BH_4)_3$ with ethylenediamine have also been reported recently [51]. Various compositions of Al$[BH_4]_3$: nC$_2$H$_4$N$_2$ were proposed according to the addition reactions:

$$Al(BH_4)_3 + nC_2H_4N_2 \rightarrow Al(BH_4)_3: nC_2H_4N_2$$  \hspace{1cm} integer $n < 6$  \hspace{1cm} (13)

$$Al(BH_4)_3 + Al(BH_4)_3: nC_2H_4N_2 \rightarrow Al(BH_4)_3: mC_2H_4N_2, m < n$$  \hspace{1cm} (14)

The structure of these adducts are not known, except for $n = 4$ [52], however the nature of $Al(BH_4)_3: nC_2H_4N_2$ is supposed
to be ionic. The ligand may be chelating and/or bridging depending on the stoichiometry, like in C₂H₄N₂ complexes with Mg(BH₄)₂ [53]. A complex with low ligand-to-metal ratio, Al(BH₄)₃·nC₂H₄N₂ (n = 1/2), was observed in our most recent work [22], where C₂H₄N₂ was generated in low concentrations upon the decomposition of its borane complex:

2Al(BH₄)₃ + (CH₂)₃N·BH₃ → [Al(CH₂)₃N·BH₃]₂ + Al(BH₄)₃ + B₃H₆ (15)

Numerous molecular dimer complexes can be obtained from ammine boranes and chlorides with AlX₃ as well as BH₃ and Al(BH₄)₃ in toluene solution. The latter yields a dimer solvate complex [HAI(BH₄)₃(TEDA) PhMe₂] [55]. The other dimers, [H(X)AlNEt₂]₂ and [Al(BH₄)₄], were obtained recently by the following reactions [56]:

2HAlOEt₂ + 2LiCl → [Cl₂AlNEt₂]₂ + 2LiCl (16)

[Cl₂AlNEt₂]₂ + 4LiBH₄ → [(BH₄)₂AlNEt₂]₂ + 4LiCl (17)

2HAIOEt₂ + 2LiNEt₂ → [H(Cl)AlNEt₂]₂ + 2LiCl (18)

2H(Cl)AlNEt₂ + 2LiBH₄ → [H(BH₄)AlNEt₂]₂ + 2LiCl (19)

The formation of stable chelate complexes is not the only way to stabilize Al(BH₄)₃ in a cationic form. In contrast to the reaction (12), an excess of NH₃ over Al(BH₄)₃ yields Al(NH₃)₆·B₂H₆ (15), which on the basis of its crystal structure can be written as [Al(NH₃)₆][BH₄]₃ (16). This complex was obtained from a solution of NH₃BH₃ in liquid NH₃, where Al is used as a dissolving anode [57].

3NaBH₄ + Al + 6NH₃ → [Al(NH₃)₆][BH₄]₃ + 3Na (20)

Interestingly, the stable [Al(NH₃)₆][BH₄]₃ can be obtained in safe conditions: it forms during the electrolysis of alkali metal borohydrides in liquid NH₃, where Al is used as a dissolving anode [57]:

Al(BH₄)₃ + 6NH₃ → [Al(NH₃)₆][BH₄]₃ (21)

Similarly to the reaction (14), a series of Al(BH₄)₃ ammoniates can be obtained by mixing the borohydride with [Al(NH₃)₆][BH₄]₃ [58]:

n[Al(BH₄)₃] + [Al(NH₃)₆][BH₄]₃ → (n + 1)[Al(NH₃)₆][BH₄]₃ (22)

The cationic form of [Al(NH₃)₆]³⁺ is stable: the mechanical reaction of [Al(NH₃)₆][BH₄]₃ with LiBH₄ gives a bimetallic complex possessing the same complex cation [27]:

[Al(NH₃)₆][BH₄]₃ + 2LiBH₄ → [Al(NH₃)₆][Li₂(BH₄)₃] (23)

The interaction of other M[BH₄]₃ (M = Na⁺, n = 1; M = Ca²⁺ and Mg²⁺, n = 2) with [Al(NH₃)₆][BH₄]₃ gives poorly crystalline products with unknown composition [59].

Remarkably, [Al(NH₃)₆][Li₂(BH₄)₃] is also quite reactive with other molecules. In particular, it forms a complex with ammonia borane, [Al(NH₃)₆][Li₂(BH₄)₃]·3NH₃·BH₃, in the mechanochanical reaction [28]:

[Al(NH₃)₆][Li₂(BH₄)₃]·3NH₃·BH₃ + 3NH₃BH₃ → [Al(NH₃)₆][Li₂(BH₄)₃]·3NH₃·BH₃ (24)

The first example of aluminium amidoborane ammoniate with suggested composition [Al(NH₃)₆][Al(NH₂)₄] was published recently [60]. The reported composition and the molecular structure were based on MAS ²⁷Al NMR spectroscopy data. This complex was obtained from a solution of NH₃BH₃·nNH₃ (n = 1–6) and AlH₃·OEt₂:

2AlH₃·OEt₂ + 6NH₃·BH₃·nNH₃ → [Al(NH₃)₆]₆ [Al(NH₃)₆]₆·6(n–1)NH₃ + 2OEt₂ + 6H₂ (25)

Crystal structures of Al–B and Al–N complex hydrides

Crystal structures of hydrides with Al–B and Al–N complex anions

Four types of aluminium complex hydrides are known to date: alanates AlH₄⁺ and AlH₄⁻, aluminium amides [Al(NH₃)₄]⁺, borohydrides [Al(BH₄)₄]⁻ and amidoboranes [Al(NH₂BH₃)₄]⁻. The details of their crystal structures are given in Table 1 and the representation of metal cation coordinations is shown in Fig. 1.

In general, complex aluminium amides are analogous to metal alanates, where all atoms of hydrogen in the AlH₄ tetrahedra are substituted by NH₃, forming the complex anion [Al(NH₃)₄]⁻. Metal cations can be linked to [Al(NH₃)₄]⁻ by nitrogen atoms via corners or edges of the complex anion. The coordination numbers of M⁺ cations in M[Al(NH₃)₄]ₙ decrease, compared to the corresponding MAIH₄ from 5 to 4 for Li⁺; from 8 to 4 for Na⁺; from 10 to 8 and 6 for K⁺, Ca⁺ and Ba⁺ [Al(NH₃)₄]⁺; respectively; from 8 to 7 for Ca²⁺. The analysis of the M–N interatomic distances reveals their linear correlation, with an effective ionic radii of the metal similar to the M–H distances in alanates [18].

Borohydrides containing complex anions [M⁺⁺(BH₄)ₙ(n–e)⁻] are generally constructed by the packing of counter-cations (or complex cations) and complex anions in close-packed inorganic structure types well known amongst the AMO₄ (A = alkali metal) oxide family [61]. However, the mixed-metal [Li₃(BH₄)₃][Al(BH₄)₃] has a unique crystal structure with respect to the [M(BH₄)₄] series. The complex cation [Li₃(BH₄)₃]³⁺ and anion [Al(BH₄)₄]⁻ are packed similar to the Frank-Kasper Cr₃Si-type phase, see Fig. 1. A topological analysis indicates that [Li₃(BH₄)][Al(BH₄)₄]₃ is an antitype of Ag₅PO₄.
The crystal structure of Na[Al(NH2BH3)4] is the only one known to date for aluminium amidoboranes [24]. The central Al3+ atom has a tetrahedral environment formed by four nitrogen atoms from four NH2BH3 anions (Fig. 1), similar to aluminium amides. The Na+ atoms are octahedrally coordinated by six BH3 groups arising from six NH2BH3. This coordination is different from M[Al(NH2)4]n, where cations are directly linked with NH2 groups. Thus, all NH2BH3 anions exhibit a bridging coordination mode linking Al3+ and Na+ cations with the formation of a 3D polymer structure. Remarkably, the dihydrogen N–H+...H–B–B bonds in Na[Al(NH2BH3)4] (1.96(1)–2.28(1) Å from XRPD and 1.92–2.34 Å from DFT) are close to the shortest dihydrogen bonds (1.91(5) Å) in a pristine AB [66], and significantly shorter compared to all known metal ammonia boranes (MABs) [24].

\[ \text{Crystal structures of molecular and cationic Al–B and Al–N complex hydrides} \]

Most crystal structures of these two classes of compounds were characterized recently (2011–2015), see Table 2, and are based on the addition reaction between Al(BH4)3 and other hydrides, like NH3, AB and LiBH4.

Table 1 Crystal structure data for hydrides with Al–B and Al–N complex anions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Cell parameters, Å</th>
<th>a, b, c (°)</th>
<th>V/Å³</th>
<th>Z</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M[Al(NH3)4]6</td>
<td>P2/n</td>
<td>9.478(1) 7.351(1) 7.398(1)</td>
<td>90.26(1) 519.39</td>
<td>4</td>
<td>[67]</td>
<td></td>
</tr>
<tr>
<td>Li[Al(NH3)4]4</td>
<td>P2/n</td>
<td>9.5075(5) 7.3610(2) 7.4076(2)</td>
<td>90.165(3)</td>
<td>4</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>Na[Al(NH3)4]4</td>
<td>P2/c</td>
<td>7.3287(2) 6.0472(2) 13.1513(2)</td>
<td>94.04(1) 581.3</td>
<td>4</td>
<td>[68]</td>
<td></td>
</tr>
<tr>
<td>Na[Al(NH3)4]2</td>
<td>P2/c</td>
<td>7.3317(9) 6.0447(8) 13.1512(2)</td>
<td>94.110(9)</td>
<td>4</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>Na2Al(NH3)4</td>
<td>Cmma or Abm2</td>
<td>23.56 19.36 6.78</td>
<td>3092.5</td>
<td>16</td>
<td>[69]</td>
<td></td>
</tr>
<tr>
<td>α-K[Al(NH3)4]4</td>
<td>C2221</td>
<td>10.00(1) 6.05(1) 10.14(2)</td>
<td>588.12</td>
<td>4</td>
<td>[70]</td>
<td></td>
</tr>
<tr>
<td>β-K[Al(NH3)4]4</td>
<td>Pnna</td>
<td>11.37(1) 8.85(1) 6.1466(6)</td>
<td>618.44</td>
<td>4</td>
<td>[35]</td>
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</tr>
<tr>
<td>β-K[Al(ND3)4]4</td>
<td>Pnna</td>
<td>11.4183(4) 8.8588(2) 6.1696(2)</td>
<td>4</td>
<td>[20]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb[Al(NH3)4]4</td>
<td>Pn/a</td>
<td>7.4064(4) 7.4064(4) 5.3864(4)</td>
<td>295.42</td>
<td>2</td>
<td>[71]</td>
<td></td>
</tr>
<tr>
<td>Cs[Al(NH3)4]4</td>
<td>Pn/a</td>
<td>7.5633(5) 7.5633(5) 5.3541(1)</td>
<td>306.24</td>
<td>2</td>
<td>[71]</td>
<td></td>
</tr>
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<td>Mg[Al(NH2)4]2</td>
<td>Hex.</td>
<td>12.1 12.1 7.95</td>
<td>1008.05</td>
<td>n/a</td>
<td>[19]</td>
<td></td>
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<tr>
<td>Ca[Al(NH2)4]2</td>
<td>Pn/a</td>
<td>6.4321(2) 6.4377(2) 12.2939(3)</td>
<td>90.612(2)</td>
<td>4</td>
<td>[20]</td>
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<tr>
<td>Ca[Al(NH3)4]2</td>
<td>Pn/a</td>
<td>6.4716(5) 6.4716(5) 12.2449(4)</td>
<td>512.70</td>
<td>4</td>
<td>[72]</td>
<td></td>
</tr>
<tr>
<td>Sr[Al(NH2)4]2</td>
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<td>17.49(1) 17.49(1) 28.17(2)</td>
<td>7462.72</td>
<td>36</td>
<td>[37]</td>
<td></td>
</tr>
<tr>
<td>M[Al(BH4)4]4</td>
<td>P2/c</td>
<td>19.6259(4) 13.5317(3) 13.5206(3)</td>
<td>107.457(2) 3425.29(13)</td>
<td>16</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>[Li4(BH4)]+ [Al(BH4)4]3</td>
<td>P–43n</td>
<td>11.4622(1) 11.4622(1) 11.4622(1)</td>
<td>1505.91(3)</td>
<td>2</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>Na[Al(BH4)4]4</td>
<td>C2/c</td>
<td>9.3375(3) 11.2499(4) 8.4112(3)</td>
<td>104.706(2) 854.61(5)</td>
<td>4</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>Na[Al(BH4)4]Cl</td>
<td>Pnna</td>
<td>7.9001(4) 7.0033(3) 6.4888(3)</td>
<td>359.0(3)</td>
<td>2</td>
<td>[46]</td>
<td></td>
</tr>
<tr>
<td>K[Al(BH4)4]4</td>
<td>Fddd</td>
<td>9.4075(3) 12.4500(4) 16.6795(4)</td>
<td>1782.43(8)</td>
<td>8</td>
<td>[21]</td>
<td></td>
</tr>
<tr>
<td>NH4[Al(BH4)4]4</td>
<td>Fddd</td>
<td>9.8875(4) 12.6005(5) 14.9656(5)</td>
<td>1864.49(13)</td>
<td>8</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>Rb[Al(BH4)4]4</td>
<td>Fddd</td>
<td>9.8889(4) 13.3009(7) 14.3252(8)</td>
<td>1876.69(7)</td>
<td>8</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>Rb[Al(BH4)4]4</td>
<td>Fddd</td>
<td>9.8889(4) 13.3009(7) 14.3252(8)</td>
<td>1876.69(7)</td>
<td>8</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>Mg[Al(NH2BH3)4]4</td>
<td>Hex.</td>
<td>12.1 12.1 7.95</td>
<td>1008.05</td>
<td>n/a</td>
<td>[19]</td>
<td></td>
</tr>
<tr>
<td>Na[Al(NH2BH3)4]4</td>
<td>P–1</td>
<td>9.4350(2) 7.7196(2) 7.6252(2)</td>
<td>97.2192(2)</td>
<td>519.88(2)</td>
<td>2</td>
<td>[24]</td>
</tr>
</tbody>
</table>

*n/a – data is not available.

The complexes of M[Al(BH4)4] contain the same bulky [Al(BH4)4]– anion with strongly deformed tetrahedral configuration, where aluminium atoms are coordinated to four BH3 groups via the BH2 edges. In contrast to M–N bonding in M [Al(NH3)4]n the coordination of metal cations in [Al(BH4)4]– exhibits bridging M–H–B character. Moreover, the borohydride group acts like a nearly linear bridging ligand with an Al–B–M angle close to 180°. This coordination behavior is usual for the framework structures of numerous other borohydrides, like the polymorphs of Mg(BH4)2 [64,65]. These topologies are typical for coordination frameworks, highlighting the role of the borohydride anion acting as the bridging directional ligand [34].

Similarly to aluminium amides, complex anions [Al(BH4)4]– can be coordinated to M+ both via corners or edges. The coordination numbers of metal cations in M [Al(BH4)4] are similar (for Li+, K+, Cs+) or higher (for Na+) than in the corresponding M[Al(NH3)4]. The crystal structure of NH3[Al(BH4)4] is identical to K[Al(BH4)4] and Rb[Al(BH4)4], which is in accordance to the similar size of the cations. However, it also contains dihydrogen H+...H–B–B bonds between protons and hydridic hydrogens of NH3 and BH4 groups. This structural feature provokes easier hydrogen comproportionation and makes it the least stable among the M[Al(BH4)4] compounds.
Equimolar amounts of NH3, AB or MeAB (methyl ammonia borane) with Al(BH4)3 result in molecular complexes [Al(NH3)(BH4)3], [Al(NH3BH3)(BH4)3] and [Al(CH3NH2BH3)(BH4)3], see Fig. 2. Similar to the [Al(BH4)4]e anion, the central Al3+ cation is linked via BH2 edges to three BH4e anions and to one molecule of NH3, AB or MeAB. The molecule of NH3 is linked to Al3+ via a nitrogen atom, which donates its lonepair electrons to Al3+, while AB and MeAB are linked via BH2 edges, all adopting a distorted tetrahedral coordination for Al3+. The resulting AlH8 polyhedron in [Al(NH3BH3)(BH4)3] and [Al(CH3NH2BH3)(BH4)3] has a shape of a snub disphenoid (one of the Johnson solids), as Mg2+ in Mg(BH4)2 structures [64,65]. Weak dihydrogen N^MeH^+/H^+ bonds associate these complexes into a 3D structure.

An increasing amount of NH3 replaces the borohydride ligands forming hexamminealuminium (III) [Al(NH3)6]3+.

Fig. 1 – Coordination of metal cations in alanates, aluminium amides, borohydrides and amidoboranes. Aluminium-centered complex anions are shown as polyhedra.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Cell parameters, Å</th>
<th>a, b, c (Å)</th>
<th>V/Å³</th>
<th>Z</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Al(NH3)(BH4)3]</td>
<td>P21/n</td>
<td>11.20(3) 11.48(3) 12.00(3)</td>
<td>100.9(5)</td>
<td>1515.0(7)</td>
<td>8</td>
<td>[50]</td>
</tr>
<tr>
<td>[Al(NH3BH3)(BH4)3]</td>
<td>P21/c</td>
<td>7.8585(2) 6.8647(1) 15.7136(8)</td>
<td>96.43(1)</td>
<td>842.36(5)</td>
<td>4</td>
<td>[25]</td>
</tr>
<tr>
<td>[Al(CH3NH2BH3)(BH4)3]</td>
<td>P̅1</td>
<td>6.2764(3) 7.9566(5) 10.3058(8)</td>
<td>70.277(7)</td>
<td>467.28(6)</td>
<td>2</td>
<td>[22]</td>
</tr>
<tr>
<td>[Al(NH3)6][BH4]3</td>
<td>Pbcn</td>
<td>13.2824(5) 15.2698(7) 13.1848(6)</td>
<td>12617.7(5)</td>
<td>12617.7(5)</td>
<td>16</td>
<td>[28]</td>
</tr>
<tr>
<td>[Al(NH3)6][Li2(BH4)5]</td>
<td>P - 3c</td>
<td>7.7978(1) 7.7978(1) 15.9693(2)</td>
<td>840.93(1)</td>
<td>840.93(1)</td>
<td>2</td>
<td>[27]</td>
</tr>
<tr>
<td>[Al(CH3NH2BH3)3][3NH3BH3]</td>
<td>F23</td>
<td>23.1220(3) 23.1220(3) 23.1220(3)</td>
<td>12361.7(5)</td>
<td>12361.7(5)</td>
<td>16</td>
<td>[28]</td>
</tr>
<tr>
<td>[Al(CH3NH2BH3)(BH4)3][AlCl4]</td>
<td>Pbca</td>
<td>12.5826(5) 12.6510(5) 20.4039(8)</td>
<td>3247.9(2)</td>
<td>3247.9(2)</td>
<td>2</td>
<td>[22]</td>
</tr>
<tr>
<td>[Al(CH2NH2BH3)(BH4)3][Al(BH4)4]</td>
<td>P21/c</td>
<td>8.4168(5) 12.0021(7) 16.2933(12)</td>
<td>101.89(1)</td>
<td>1610.7(2)</td>
<td>4</td>
<td>[22]</td>
</tr>
<tr>
<td>[SiCl2AlNEt2]2</td>
<td>Pnma</td>
<td>13.0763(8) 10.5499(8) 11.6434(8)</td>
<td>2674.14</td>
<td>2674.14</td>
<td>8</td>
<td>[59]</td>
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<tr>
<td>[Cl2AlNEt2]2</td>
<td>Pnma</td>
<td>12.0647(8) 10.4815(6) 11.4958(7)</td>
<td>1606.3(2)</td>
<td>1606.3(2)</td>
<td>4</td>
<td>[56]</td>
</tr>
<tr>
<td>[H(BH4)AlNEt2]2</td>
<td>C2/c</td>
<td>8.7545(5) 13.0364(7) 15.9026(9)</td>
<td>93.884(3)</td>
<td>1810.8(2)</td>
<td>4</td>
<td>[56]</td>
</tr>
<tr>
<td>[H(BH4)AlNEt2]2</td>
<td>Pnma</td>
<td>12.1579(14) 10.3264(12) 12.2729(14)</td>
<td>1540.8(3)</td>
<td>1540.8(3)</td>
<td>4</td>
<td>[56]</td>
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</table>
complex cation, passing from the molecular structure to ionic. This complex cation has a distorted octahedral coordination of $\text{Al}^{3+}$, linked exclusively with six $\text{NH}_3$ ligands via nitrogen atoms. The hexamminealuminium cations in $[\text{Al}(\text{NH}_3)_6][\text{BH}_4]^-$ are surrounded by free $\text{BH}_4^-$ anions, connected with $\text{NH}_3$ by dihydrogen bonds at $1.91\text{ Å}$.

The insertion of Li$\text{BH}_4$ into $[\text{Al}(\text{NH}_3)_6][\text{BH}_4]^-$ yields a Li$^+$ based anion and the resulting formula $[\text{Al}(\text{NH}_3)_6][\text{Li}_2(\text{BH}_4)_5]^-$ [27]. The $[\text{Al}(\text{NH}_3)_6]^{3+}$ complex cation remains in the structure without significant changes and Li$^+$ adopts tetrahedral coordination by four $\text{BH}_4^-$ groups in line with lithium borohydride crystal chemistry [73]. These Li$\text{BH}_4^-$ tetrahedra are then vertex-linked through three bridging $\text{BH}_4^-$ units with the fourth one in the trans position, leading to the formation of a two-dimensional honeycomb-patterned sheet, see Fig. 2 [27].

This structural topology is similar to borohydride structures, as in Mg($\text{BH}_4$)$_2$ polymorphs [64,65], as well as to that of some porous silicate zeolites [74]. As in Na[$\text{Al}(\text{NH}_3\text{BH}_3)_4$], the closest $\text{N}^-$–$\text{H}^+$–$\text{H}^+$–$\text{B}$ interactions in $[\text{Al}(\text{NH}_3)_6][\text{Li}_2(\text{BH}_4)_5]$ are even shorter than those in MABs and are comparable to those in the solid ammonia borane, $\text{NH}_3\text{BH}_3$ [24,66].

Interestingly, $[\text{Al}(\text{NH}_3)_6][\text{Li}_2(\text{BH}_4)_5]$ is not the last member of the addition sequence (Fig. 2), as it reacts further with $\text{AB}$ forming $[\text{Al}(\text{NH}_3)_6][\text{Li}_2(\text{BH}_4)_5]\cdot 3\text{NH}_3\text{BH}_3$. $\text{Al}^{3+}$ is identically coordinated to six ammonia atoms in hexamminealuminium (III) complex cation. On the contrary, the coordination behavior of Li atoms changes dramatically: one Li$^+$ is coordinated to $[\text{Al}(\text{NH}_3)_6]^{3+}$ octahedron via the face, while the other Li$^+$ adopts tetrahedral coordination with one $\text{BH}_4^-$ and three molecules of $\text{AB}$. Non-coordinated $\text{BH}_4^-$ anions fill the space in the vicinity of $[\text{Al}(\text{NH}_3)_6]^{3+}$, forming $\text{H}^+$–$\text{H}$ dihydrogen bonds with $\text{NH}_3$ and $\text{AB}$ molecules. The intermolecular $\text{H}^+$–$\text{H}$ distances of 1.90 and 1.79 Å are found to be slightly shorter than those in the recently discovered amino metal borohydrides (AMBs) and MABs [75].

Given the description above, the formula of this compound is better written as $[\text{LiAl}(\text{NH}_3)_6]([\text{Li}\text{NH}_3\text{BH}_3][\text{BH}_4]^+)[\text{BH}_4]^-$.

The examples of complex hydrides where aluminium atoms are centering both the complex cation and anion are quite rare. Indeed, only two structures of “autoionized” Al-based hydrides, $[\text{Al}(\text{CH}_3\text{NH}_2\text{BH}_3)_2\text{Cl}_2][\text{AlCl}_4]$ and $[\text{Al}(\text{CH}_2\text{NH}_2\text{BH}_3)_2][\text{Al}(\text{BH}_4)_4]$, were recently investigated, see Fig. 3.

Me$\text{AB}$ ligand coordinates to $\text{Al}^{3+}$ via bridging hydrogens of the $\text{BH}_3$ groups with $\text{Al}$–$\text{B}$ and $\text{Al}$–$\text{H}$ distances of 2.24(5)–2.25(4) and 1.8(2)–1.9(2) Å, which are similar to the ones in molecular $[\text{Al}(\text{NH}_3\text{BH}_3)[\text{BH}_4]^+]$ and $[\text{Al}(\text{CH}_3\text{NH}_2\text{BH}_3)[\text{BH}_4]^+]$ complexes. The $\text{Al}$–$\text{Cl}$ distances of 2.11(1) and 2.14(1) Å in the $[\text{Al}(\text{CH}_3\text{NH}_2\text{BH}_3)_2\text{Cl}_2]^-$ cation are in a good agreement with 2.1–2.3 Å from other known cationic complexes of $\text{Al}$ [76].
[Al(CH₂NH₂)₂(BH₄)₂][Al(BH₄)₄] is the only autoionized Al-borohydride complex known so far. Each of its ions adopts a distorted tetrahedral coordination for Al atoms. The N/Al/N angle of 86.5(2)° is similar to other known bidentate chelates of Al [76]. The geometry of a slightly flattened tetrahedron for [Al(BH₄)₄]⁻ complex anion is also identical to those in M[Al(BH₄)₄] (M = Li⁺, Na⁺, K⁺, NH₄⁺, Rb⁺, Cs⁺) and [Ph₃MeP][Al(BH₄)₄] [22,77].

[Al(CH₂NH₂)₂(BH₄)₂]⁺ is a chelate, where Al atom is linked via N atoms to the same ethylenediamine molecule, and via BH₂ edges to two BH₄ groups, see Fig. 3. Al–B distances of 2.16(7) and 2.17(8) Å in the cation are slightly shorter than 2.23(8)–2.27(8) Å Al–B distances in [Al(BH₄)₄]⁻. The Al–N distances of 1.95(4) and 1.96(4) Å are typical (1.9–2.0 Å) for other Al-containing cations [76]. Similarly to the molecular [Al(NH₃BH₃)(BH₄)₃] and [Al(CH₃NH₂BH₃)(BH₄)₃], the crystal structure of [Al(CH₂NH₂)₂(BH₄)₂][Al(BH₄)₄] contains both simple and bifurcated dihydrogen N–H⁺…H⁻–B bonds with H–H distances of 2.02–2.22 Å and H–H–N angles of 140–160°.

Molecular hydride complexes of Al can also take a dimeric form, forming (Al–H)₂ and (Al–N)₂, four-membered rings [55,56]. The bridging Al–(μ-H)₄–Al is present in the crystal structure of [HAl(BH₄)₂(TEDA)BH₃](PhMe)₂, see Fig. 4a [55]. Similar Al–(μ-H)–Al units have been proposed for [HAl(BH₄)₂]n from NMR and IR spectroscopy data [78]. The reported interatomic distances Al–N, Al–B, B–N and Al–H (with BH₄) are similar to those in M[Al(BH₄)₄] and [Al(NH₃BH₃)(BH₄)₃]. The Al–H distance with the bridging hydrogen is slightly shorter, 1.72 Å, than the Al–H bond with the BH₄ group of around 1.82 Å. It was surmised that the crystal structure might be stabilized by π-interactions and weak dihydrogen N–H⁺...H⁻–B bonds with H–H distances of ~2.7–2.9 Å [55].

The crystal structures of [X₂AlNEt₃]₂ and [H(X)AlNEt₃]₂ (X = Cl⁻, BH₄⁻) contain (Al–N)₂ four-membered rings [56], see Fig. 4b and c. The Al–N–Al–N torsion angles showed the stronger deviation from planarity in the presence of chlorine ligands due to the steric and electron drawing effect on Al atoms [56].

### Thermal decomposition and hydrogen storage properties of Al–B and Al–N complex hydrides

Thermal properties of complex hydrides with Al–B and Al–N anions

M[Al(NH₂)₄]n complexes show peaks of ammonia release at temperatures from 70 to 160 °C [19]. The decomposition temperatures for M[Al(NH₂)₄]n series increases with the electronegativity of M, i.e. from K to Li and from Ca to Mg. This trend is opposite for metal borohydrides, M(BH₄)n [79,80], as well as for Al-based bimetallic series, M[Al(BH₄)₄], as will be discussed below. The opposite trends apparently reflect different mechanisms of the decomposition of the amide and borohydride series.

There are several interpretations regarding the thermal decomposition pathway of alkali metal aluminium amides. The most detailed investigation has been done for Li[Al(NH₂)₄]. The first attempt to explain the thermal decomposition of Li...
Various formation steps are also complicated. Possible formation of composite was explained by the rapid decomposition of this compound remains unclear. The poor reversibility of the pristine LiAl(NH2)4, the nature of the LiAl(NH)2 metastable species correspond to the amorphous Li2NH, the Eymery et al. combines some part from the scheme (22), but the final Li-containing decomposition:

\[
\text{Li}[\text{Al(NH}_2\text{)}_4]_n \rightarrow \text{LiAl(NH}_2\text{)}_2 + 2\text{NH}_3 \\
\rightarrow 1/3\text{Li}_3\text{AlN}_2 + 2/3\text{AlN} + 8/3\text{NH}_3 \\
\text{ (160 – 185 °C)} \\
\rightarrow 1/3\text{Li}_3\text{AlN}_2 + 2/3\text{AlN} + 8/3\text{NH}_3 \\
\text{ (160 – 185 °C)} \\
\text{ (26)}
\]

Jacobs at al. proposed another scheme, via formation of LiNH2:

\[
\text{Li}[\text{Al(NH}_2\text{)}_4]_n \rightarrow \text{LiNH}_2 + 1/2\text{Al}_2(\text{NH}_2)_3 + 3/2\text{NH}_3 \\
\rightarrow \text{LiNH}_2 + \text{AlN} + 2\text{NH}_3 \\
\rightarrow 1/3\text{Li}_3\text{AlN}_2 + 2/3\text{AlN} + 8/3\text{NH}_3 \\
\text{ (160 – 280 °C)} \\
\rightarrow 1/3\text{Li}_3\text{AlN}_2 + 2/3\text{AlN} + 8/3\text{NH}_3 \\
\text{ (400 °C)}
\]

More recent investigation from Eymery et al. combines (27)

Formation of the crystalline and amorphous Li3AlN2 and Li2NH1 anions was suggested upon the thermal decomposition [83,84]:

\[
\text{Li}[\text{Al(NH}_2\text{)}_4]_n \rightarrow \text{Li}_3\text{Al}_3(\text{NH}_2)_{12} - 2\text{Al}(\text{NH}_2) + \text{NH}_3 \\
\rightarrow \text{Li}_3\text{Al}_3(\text{NH}_2)_4 - m(\text{NH}_2)_{4 - m} \text{N}_m + (4 + m)\text{NH}_3 \\
\rightarrow (1 - n)\text{Li}_3\text{AlN}_2 + 2(1 - n)\text{AlN} + \text{Li}_3\text{Al}_3\text{N}_m + 8\text{NH}_3
\]

\text{ (28)}

Despite the lack of hydrogen evolution from the pristine M [Al(NH3)4] complexes, the interest remains in their RHCs with other metal hydrides. In particular, Li[Al(NH3)4]–4LiH composite showed hydrogen desorption already at room temperature, according to the proposed reaction [85]:

\[
\text{Li}[\text{Al(NH}_3\text{)}_4]_4 + 4\text{LiH} \rightarrow \text{Li}_2\text{Al(NH}_3\text{)}_2 + 2\text{Li}_2\text{NH} + 4\text{H}_2 \\
\text{ (29)}
\]

Fig. 5 – The experimental decomposition temperatures of metal borohydrides as a function of ionic potential obtained using dynamical charges on cations. The values for M[Al(BH4)4] (M = Li+, Na+, K+, Rb+, Cs+) are shown as red circles, while the data shown in black circles were taken from Ref. [86]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

storing larger amounts of hydrogen at temperatures around 100 °C.

The experimental decomposition temperatures of M [Al(BH4)4] (M = Li+, Na+, K+, Rb+, Cs+) linearly correlates with the square root of their ionic potential \( \phi^{0.5} \) on M, calculated from the dynamical charges, see Fig. 5 [22]. This parameter gives a more linear correlation with the decomposition temperatures than the Pauling electronegativity, \( x_p \). NH4[Al(BH4)4] does not fall on in this line, because the recombination of hydrogens from NH4 and BH4 lowers significantly the stability of this compound.

In terms of thermal decomposition properties, the family of M[Al(BH4)4] (M = Li+, Na+, K+, NH4, Rb+, Cs+) and [Li4(BH4)][Al(BH4)4]3 can be separated into several groups: the decomposition of light (Li+, Na+), medium (K+), heavy (Rb+, Cs+) and proton-containing (NH4) aluminium borohydrides.

The light M[Al(BH4)4] (M = Li+, Na+) decompose below 100 °C with the evolution of molecular Al(BH4)3 [22,41,87]:

\[
M[\text{Al(BH}_4\text{)}_4] \rightarrow \text{MBH}_4 + \text{Al(BH}_4\text{)}_3 \text{ (M = Li+, Na+)}
\]
Interestingly, Li[Al(BH$_4$)$_4$] decomposes into [Li$_4$(BH$_4$)] [Al(BH$_4$)$_3$] at the first step and the latter gives the starting LiBH$_4$ and the rest of Al(BH$_4$)$_3$ [22]:

\[
[Li_4(BH_4)][Al(BH_4)_3] \rightarrow 4LiBH_4 + 3Al(BH_4)_3
\]  

(32)

4Li[Al(BH$_4$)$_4$] → [Li$_4$(BH$_4$)][Al(BH$_4$)$_3$] + Al(BH$_4$)$_3$  

(33)

K[Al(BH$_4$)$_4$] decomposes at around 160 °C and two different decomposition schemes have been proposed. Among the possible decomposition reactions, one is identical to the decomposition of the light alkali metal aluminium borohydrides (27), with evolution of Al(BH$_4$)$_3$ and formation of KBH$_4$ [42,43]. Due to the evolution of hydrogen and diborane during thermal decomposition and due to lower mass losses than expected for Al(BH$_4$)$_3$ abstraction, a different decomposition pathway has been proposed according to the following reaction [21]:

\[
2K[Al(BH_4)_4] \rightarrow KBH_4 + \text{amorphous "KAi}_{3}B_7" + 2B_2H_6 + 8H_2
\]  

(34)

The thermal decomposition of heavy M[Al(BH$_4$)$_4$] (M = Rb$^+$, Cs$^+$) gives the lowest mass losses. The presence of hydrogen and diborane was confirmed by thermogravimetric analysis coupled with mass spectrometry analysis of evolving gases (TGA–MS), however the decomposition scheme is not defined with certainty [21]. Remarkably, Cs[Al(BH$_4$)$_4$] evolves the pure hydrogen in the M[Al(BH$_4$)$_4$] series, at temperatures below 160 °C.

NH$_4$[Al(BH$_4$)$_4$] decomposes in two steps [22], at about 35 °C and 58 °C. A similar two-step thermal decomposition was found for [Al(NH$_2$BH$_4$)(BH$_4$)$_3$] [25], which will be discussed later. According to the TGA–MS data, NH$_4$[Al(BH$_4$)$_4$] releases hydrogen, diborane and ammonia at both decomposition steps. The solution $^{11}$B and $^{27}$Al NMR spectra showed also the signals of diborane, Al(BH$_4$)$_3$, Al(BH$_4$)$_3$, NH$\text{B}$ and [HAl(BH$_4$)$_4$] [22,25].

The Al-based bimetallic compounds combining even stronger polarizing Mg$^{2+}$ or Ca$^{2+}$ cations, would lead to the decomposition at room temperature, and thus are most likely unstable under ambient conditions. Indeed, the attempts to isolate bimetallic borohydrides of the Mg$_3$[Al(BH$_4$)$_4$], Al$_3$[Al(BH$_4$)$_4$] and Ca$_3$(BH$_4$)$_2$: Al(BH$_4$)$_3$ systems were unsuccessful [22]. Consequently, the family of Al-based borohydrides is limited likely to the alkali metal and ammonium series. With the diversity of the decomposition pathways and the varied stability, the aluminium borohydride chemistry can be developed in terms of reactive hydride composites based on M[Al(BH$_4$)$_4$], similarly to $M[Al(NH_2)BH_4]$. As we mentioned above in this subchapter, the M[Al(NH$_2$)BH$_4$] ($M = Mg^{2+}, Ca^{2+}$) series is on the contrary stable, with higher stability for the strongest polarizing Mg$^{2+}$.

Na[Al(NH$_2$BH$_4$)$_4$] is a completely different representative possessing an Al-based complex anion, since it has an anion containing intermolecular dihydrogen N–H$^+$ ... H$^+–$B bonds. The thermal decomposition of Na[Al(NH$_2$BH$_4$)$_4$] occurs in two steps at around 120 and 160 °C and reveals the formation of only one crystalline phase, NaBH$_4$ [24]. The FTIR spectrum of the final residue shows characteristic bands of NaBH$_4$ and a number of additional bands suggesting the presence of the Al–N, B–N, B–H and N–H bonds. Using TGA–MS and volumetric data on the decomposition of Na[Al(NH$_2$BH$_4$)$_4$], the overall reaction was suggested:

\[
\text{Na}[\text{Al(NH}_2\text{BH}_4]_4 \rightarrow \text{NaBH}_4 + \text{AlN}_2\text{B}_4\text{H}_{(0.18)} + (6.2\pm8.0)\text{H}_2
\]  

(35)

Remarkably, a slow hydrogen absorption was observed at 250 °C for the completely decomposed samples of Na[Al(NH$_2$BH$_4$)$_4$] [24]. About 1.7 out of 6.2 mol (~27%) of the released hydrogen has been reabsorbed by the amorphous residue. This reversible absorption presumably corresponds to the reversibility of the second decomposition step (at 160 °C) [24].

Na[Al(NH$_2$BH$_4$)$_4$] forms quantitatively in the NaAlH$_4$–4NH$_2$BH$_3$ system, releasing 4 equivalents of hydrogen. Various composites between alanates and AB can be considered in a broader context. In particular, MAIAlH$_4$–NH$_2$BH$_3$ (M = Li$^+$, Na$^+$) as well as Li$_3$AlH$_6$–nNH$_2$BH$_3$ (3 ≤ n ≤ 6) composites have been intensively investigated [48,89]. Hydrogen desorption from MAIAlH$_4$–NH$_2$BH$_3$ (M = Li$^+$, Na$^+$) starts already at 53 and 66 °C, respectively, where the formation of the [Al(NH$_2$BH$_4$)$_4$] anion is confirmed [24]. The peak of hydrogen release from various Li$_3$AlH$_6$–nAB composites is in the range of 50–72 °C [48,89]. For the interaction between Li$_3$AlH$_6$ and AB, two possible scenarios have been suggested [48,89]. First, solid state NMR data indicate that Li$_3$AlH$_6$–3NH$_2$BH$_3$ composite undergoes a formation of (LiAl)$_x$(AB)$_{1-x}$ at the temperatures as low as 50 °C and a subsequent polymerization [89]. Second, the recent investigation of Li$_3$AlH$_6$–4NH$_2$BH$_3$ suggested the formation of a mixed-metal amidoborane, with a proposed composition Li$_3$AlH$_6$($n$NH$_2$BH$_3$)$_4$ [48]. 9 wt% of hydrogen evolves from Li$_3$AlH$_6$–4NH$_2$BH$_3$ within 200 min at 130 °C [48]. The TGA and MS data also confirmed the high purity of hydrogen from the Li$_3$AlH$_6$–nNH$_2$BH$_3$ (n = 4 and 5) composites, highlighting an effective suppression of multiple volatile byproducts of ammonia, borazine and aminoborane NH$\text{B}$H$_2$, which is usual for the dehydrogenation of pristine AB [90,91]. Moreover, the hydrogen desorption capacity of the Li$_3$AlH$_6$–4NH$_2$BH$_3$ system can be regenerated with 35% yield by a chemical treatment with hydrazine [48].

**Thermal properties of molecular and cation Al–B and Al–N complex hydrides**

Most examples of these two classes of materials contain protic and hydric hydrides present in N–H$^+$ and B–H$^+$ groups, whereby this combination favors hydrogen release at moderate temperatures. Numerous composites with chemical hydrides, such as AB, have been intensively studied and showed good dehydrogenation properties. The molecular complex [Al(NH$_2$BH$_4$)(BH$_4$)$_3$] demonstrates two decomposition steps: the first starts at ~60 °C and finishes at ~80 °C, the second is centered around 90 °C, see Table 3 [25]. The first step is endothermic (39 kJ/mol) and can be separated from the second by carrying out the reaction at 70 °C. Remarkably, TGA–MS data, volumetric analysis and solution $^{11}$B and $^{27}$Al NMR confirmed the evolution of 2 mol of pure hydrogen at 70 °C in accordance with a reaction:
This favorable decomposition pathway, endothermic dehydrogenation and low decomposition temperature, make this system an attractive model for efficient hydrogen elimination from AB. Al(BH$_4$)$_3$ works as a unique mild Lewis acid, which coordinates both the starting and the dehydrogenated BH$_n$ groups ($n = 1, 3$). In perspective, other Al-based Lewis acids, less challenging with respect to stability and safety than aluminium borohydride, can be used for the dehydrogenation of AB and its derivatives.

The series of Al(BH$_4$)$_3$·$n$C$_2$H$_8$N$_2$ (1/$n$C$_2$H$_8$N$_2$) have also been characterized in terms of hydrogen storage properties [51], the details of which are shown in Table 3. Two-step dehydrogenation is typical for these complexes, where H$_2$ is the predominant product according to the MS experiments. According to the temperature-programmed desorption, half of the total amount of H$_2$ is released during the first step; the amount of hydrogen released increases with $n$. It was pointed out that the C–H bond was not involved in the dehydrogenation of the complex. It was suggested that one of the two amino groups combines with some of the BH$_4$ anions through the combination of $\text{N}^+\text{H}^-\cdot\cdot\cdot\text{H}^+\text{B}$ dihydrogen bonds, while the second amino group reacts with BH$_4$ at higher temperatures.

The cation complex [Al(NH$_3$)$_6$]$[\text{BH}_4]$ along with its derivatives and numerous composites with LiBH$_4$ and AB has attracted significant attention by the hydrogen storage community, see Table 4. The pristine [Al(NH$_3$)$_6$]$[\text{BH}_4]$ and its derivatives have shown promising hydrogen storage properties.
composite with 2 mol of LiBH₄ release hydrogen contaminated significantly by NH₃ [26]. The second problem is related to poor dehydrogenation kinetics under moderate temperatures [26]. These disadvantages were eliminated by decreasing the ammonia content in the starting complex. This decreases the H₂ desorption temperature and improves the purity of the released gas, especially for H⁴⁺/H⁺ ratios in the composites close to one, the latter corresponds to 4:3NH₃/BH₄ molar ratio, see Table 4 [58]. The second parameter influencing hydrogen purity and the desorption temperature is the addition of other metal borohydrides [59]. In particular, Mg(BH₄)₂ has the most remarkable impact on the purity of the released hydrogen both for [Al(NH₃)₆][BH₄]₃ and [Al(NH₃)₆][Li₂(BH₄)₃]. This phenomenon was explained by the high polarizing power of Mg²⁺, which helps to compensate a relatively low polarizing power of the large [Al(NH₃)₆]³⁺ cation. It was suggested that the added cations activate the borohydride to such an extent that its hydridic hydrogens react with the protons of [Al(NH₃)₆]³⁺ cation [59]. Another possible mechanism is that strongly polarizing cations can coordinate and thus destabilize the ammonia complex [Al(NH₃)₆]³⁺.

Numerous composites of [Al(NH₃)₆][BH₄]₃ and [Al(NH₃)₆][Li₂(BH₄)₃] with AB have been investigated [28]. The addition of AB significantly lowered the onset temperature of gas evolution. The most enhanced hydrogen purity and release kinetics was observed for [Al(NH₃)₆][Li₂(BH₄)₃]−4NH₃BH₄ complex and for [Al(NH₃)₆][Li₂(BH₄)₃]−3NH₃BH₄ [28]. The H₂ evolution results from the interaction between AB and NH₃ of the [Al(NH₃)₆]³⁺ cation [28].

In order to facilitate the dehydrogenation kinetics and regeneration of [Al(NH₃)₆][BH₄]₃, its composites with AB and LiBH₄ were synthesized and a nanoconfinement strategy was also applied [28,92]. A hypercross-linked porous polymer of poly(styrene-co-divinylbenzene) (PSDB) resin was used as a nanosupport. The phenyl rings of the PSDB resin interact with the Lewis-acidic metal cations, such as Al³⁺ in the initial Al(BH₄)₃, and then lead to their anchoring. Subsequent treatment with ammonia yields well-distributed [Al(NH₃)₆][BH₄]₃ [28,92]. The nanosized Al(BH₄)₃-based materials featured an advanced hydrogen-storage performance well beyond that of its bulk counterpart. This strategy gives dehydrogenation with high purity (>99mol%), for [Al(NH₃)₆][BH₄]₃ and superior kinetics [28,92]. More importantly, dehydrogenated [Al(NH₃)₆][BH₄]₃/PSDB was partly regenerated by hydrazine, and the rehydrogenated material can be again dehydrogenated [92].

The autoionized complex [Al(NH₃)₆][Al(NH₂)₄][BH₄]₃ decomposes in the range of 65–180 °C [60]. It gives different decomposition products under inert gas flow and in a closed vessel in accordance with the following equations, respectively:

\[ [Al(NH₃)₆][Al(NH₂)₄][BH₄]₃ \rightarrow 2AlN₆B₃H₆ + 6NH₃ + 12H₂ \] (37)

\[ [Al(NH₃)₆][Al(NH₂)₄][BH₄]₃ \rightarrow 2AlN₆B₃H₆.₅ + (8.5–9.0)H₂ \] (38)

The XPS characterization of the remaining species of AlN₆B₃H₆ suggests the formation of an Al–N–B matrix with anticipated borazine-like structure [60]. On the other hand, AlN₆B₃H₆.₅ contains boron atoms with a BN₃ or BN₃H environment, which proves a different decomposition mechanism in a closed system.

Composition-structure-property relations

The comparison of the decomposition temperatures and hydrogen purities for the homoletic Al-based complexes points to the improved properties for the systems containing both protic and hydridic hydrogens, namely H⁺⁺ and H⁺³− connected to N and B atoms respectively. Despite the fact that hydrogen desorption can originate also from homopolar H⁺⁺...H⁺⁺ and H⁺³−...H⁺⁺ interactions [93], the anionic M[Al(NH₃)₆]₃ and M[Al(BH₄)₃] (M = alkali metal for n = 1, and alkali earth metal, for n = 2) in their pure form desorb ammonia, diborane and even Al[BH₄]₃. However, due to the high H-capacity, they are interesting as potential components of RHCs in combination with other hydrides, containing the counter-charged hydrogens. In particular, it would be interesting to characterize RHCs based on mixtures of M[Al(NH₃)₆]₃ with M[Al(BH₄)₃]. The formation and properties of amide-borohydride complexes like M[Al(BH₄)₄(NH₂)₃] should also be explored. The first amide-borohydride containing aluminum, Li₃(BH₄)[Al(ND₂)₄], was reported during the revision of this manuscript [94]. Interestingly, Al³⁺ coordinates only amides while the borohydride anions interact with the Li⁺ cation. The presence of boron and nitrogen atoms allows the formation of the unique decomposition products prone to rehydrogenation, direct or with the help of hydrazine [95]. Good examples are the products obtained by dehydrogenation of Na[Al(NH₂BH₃)₄] [24] and of Li₃AlH₆−4NH₃BH₄ [48] systems.

Desorption of pure hydrogen at mild conditions is favored by the presence of H⁺⁺ and H⁺³−. However, the existence of the dihydrogen bonds H⁺⁺−H⁺⁺ in the structure of the starting hydride is not a prerequisite. An example is Li₃(BH₄)(NH₃)₃ containing no dihydrogen bonds [96] but desorbing pure hydrogen at around 100 °C [97]. It would be interesting to analyze the correlation between the length of the H⁺⁺−H⁺⁺ contacts and the decomposition temperature. In Fig. 6, we plot data for all Al-based complexes with known crystal structures.
containing dihydrogen bonds, along with the pristine AB for comparison. As can be expected, compounds with the shortest H\textsuperscript{+}/H\textsuperscript{+} bonds are less stable, probably due to the easy recombination of hydrides to form H\textsubscript{2}. The dihydrogen bonds of 2.0–2.1 Å correspond to the maximum in stability of the hydrides. Although the latter observation is not rigorous considering the number of the experimental points, it is clear from the mechanistic considerations that not all dihydrogen bonds are favoring direct hydrogen splitting on heating, but all of them are stabilizing the initial complex.

Note that short dihydrogen bonds do not ensure the formation of pure hydrogen. An important parameter is also a ratio of protic and hydridic atoms H\textsuperscript{+}/H\textsuperscript{+}, because a significant excess of protic or hydridic hydrogens creates different impurities: protic – ammonia, hydridic – diborate or others, such as Al(BH\textsubscript{4})\textsubscript{3}. [Al(NH\textsubscript{2})\textsubscript{3}][Li\textsubscript{3}(BH\textsubscript{4})\textsubscript{3}] and [Al(NH\textsubscript{2})\textsubscript{3}][Li\textsubscript{3}(BH\textsubscript{4})\textsubscript{3}]·3NH\textsubscript{3}BH\textsubscript{3} contain almost equal numbers of protic and hydridic hydrides and release molecular H\textsubscript{2} with a purity higher than 94 wt%. The other possible explanation of the significant improvement of hydrogen purity, in comparison with the pristine [Al(NH\textsubscript{2})\textsubscript{3}][BH\textsubscript{4}]\textsubscript{3}, is the presence of the strongly polarizing Li\textsuperscript{+} cation [98] which destabilizes [Al(NH\textsubscript{2})\textsubscript{3}]\textsuperscript{3−}, similar to the activation made by Mg\textsuperscript{2+} [59].

Interestingly, the complexes of [Al(NH\textsubscript{2})BH\textsubscript{3}][BH\textsubscript{4}]\textsubscript{3} and Na [Al(NH\textsubscript{2})BH\textsubscript{3}]\textsubscript{3} desorb pure hydrogen, even though the H\textsuperscript{+}/H\textsuperscript{+} ratios is far from ideal. Moreover, the decomposition products of Na[Al(NH\textsubscript{2})BH\textsubscript{3}]\textsubscript{4} exhibit a partial reversibility and [Al(NH\textsubscript{2})BH\textsubscript{3}][BH\textsubscript{4}]\textsubscript{3} demonstrated an endothermic dehydrogenation, which can also be potentially reversible. These observations point out the importance of the composition of the forming products, which may hold a part of the excessive hydridic or protic hydrogens. The fundamental understanding of the composition and the chemical structure of the decomposition products remains one of the most challenging problems for the characterization of the real mechanisms of de- and re-hydrogenation in chemical hydrides.

One of the possible regeneration scenarios can be similar to the hydrogenation of Al via the formation of alanate and alane complexes with Lewis bases. In particular, the hydrogenation of aluminium is possible in the presence of the coordinating solvents, such as THF, dimethylether, dimethylamylamine (DMEA) and triethylamine (TMA) [99–102].

Conclusions and perspectives

The high polarizing power of Al\textsuperscript{3+} makes it a strong complex-forming agent, and thus it alters significantly the properties of well known hydrides, such as borohydrides, amides, amidoboranes, ammonia borane and ammonia. Effectively, Al\textsuperscript{3+} is a strong Lewis acid, serving as a template for chemical transformations involving light chemical and complex hydrides. Remarkably, aluminium is capable of coordinating both the initial hydrogenated species as well as the dehydrogenation products, enabling in some cases a hydrogen desorption reversibility. Thus, this review aims at drawing attention not to the classical Al–H interactions observed in alanates and alane, but rather to the chemistry of light hydrides templated on aluminium atoms. Nevertheless, the Al–H chemistry shares some features with the chemistry of hydrides coordinated to Al\textsuperscript{3+}: the Al atom coordinates 4 or 6 neighbours (H\textsuperscript{+} or complex hydride units such as BH\textsubscript{4} and NH\textsubscript{3} etc.) and typically forms mononuclear complexes.

Al complexes with B- and N-based hydrides were classified in this review according to the charge of the Al-based complex, as anionic, molecular, cationic or “autoionized”, whereas Al is centering both the cation and the anion. In the series of Al-based amides M[Al(NH\textsubscript{2})\textsubscript{3}]\textsubscript{n}, borohydrides M[Al(BH\textsubscript{4})\textsubscript{3}] and amidoboranes M[Al(NH\textsubscript{2}BH\textsubscript{3})\textsubscript{3}], aluminium forms tetrahedral complex anions. The shape of the [Al(BH\textsubscript{4})\textsubscript{3}]\textsuperscript{−} tetrahedron is found to be slightly flattened, as compared to the nearly ideal tetrahedral [Al(NH\textsubscript{2})\textsubscript{4}]\textsuperscript{−} and [Al(NH\textsubscript{2}BH\textsubscript{3})\textsubscript{4}]\textsuperscript{−}. The molecules of NH\textsubscript{3}, AB and their substituted derivatives, stabilize Al(BH\textsubscript{4})\textsubscript{3} in a molecular and in cationic forms. Addition of one ligand yields molecular complexes; the coordination of Al in the molecular [Al(NH\textsubscript{2})\textsubscript{3}][BH\textsubscript{4}]\textsubscript{3}, [Al(NH\textsubscript{2}BH\textsubscript{3})][BH\textsubscript{4}]\textsubscript{3} and [Al(2CH\textsubscript{2}NH\textsubscript{2}BH\textsubscript{3})][BH\textsubscript{4}]\textsubscript{3} resembles the tetrahedral coordination of Al in [Al(BH\textsubscript{4})\textsubscript{3}]\textsuperscript{−}. Larger amounts of donor nitrogen ligands displace the borohydride groups from the coordination sphere of Al, creating cation complexes, as, for example, those based on [Al(NH\textsubscript{2})\textsubscript{3}]\textsuperscript{3−} cation having the octahedral geometry.

Upon thermal decomposition, the anionic and cationic Al-based complexes evolve different gas products besides hydrogen. Different factors influencing the stability of the complexes and the hydrogen purity were analyzed in the Section Composition-structure-property relations. They include the simultaneous presence of the protic H\textsuperscript{+} and the hydridic H\textsuperscript{−} hydrogens, their atomic ratio, the presence and the lengths of the dihydrogen bonds, but above all the composition of the dehydrogenation products. The latter can retain the excess of hydridic or protic hydrogens, and most importantly favor the reversibility. In particular, we pointed out that the presence of both boron and nitrogen atoms allows the formation of unique decomposition products prone to rehydrogenation.

An excellent example where Al\textsuperscript{3+} serves as a template for the conversion of the B- and N-based hydrides is the complex of aluminium borohydride with ammonia borane, [Al(NH\textsubscript{2}BH\textsubscript{3})][BH\textsubscript{4}]\textsubscript{3} [25]. The endothermic release of two equivalents of hydrogen leads to the formation of [Al(NHBH)(BH\textsubscript{4})\textsubscript{3}]\textsubscript{n}, where the dehydrogenated ammonia borane remains coordinated to the Al atom. This encourages a search for other Al-based Lewis acids, less challenging with respect to stability and safety than aluminium borohydride. A substitution on the coordinated AB should prevent further dehydrogenation of the intermediate, and permit a thorough exploration of their reversibility. Therefore, the family of [Al(RNH\textsubscript{2}BH\textsubscript{3})X\textsubscript{3}] (X = anion) should be investigated in detail. The thermal decomposition behavior in M[Al(NH\textsubscript{2})\textsubscript{3}]\textsubscript{n} and M[Al(BH\textsubscript{4})\textsubscript{3}] anionic complexes is quite different from each other. In particular, the decomposition temperatures for M [Al(NH\textsubscript{2})\textsubscript{3}]\textsubscript{n} series increases with the electronegativity of M, while the opposite trend is observed for the borohydrides M [Al(BH\textsubscript{4})\textsubscript{3}]. Both systems contain an excess of either protic or hydridic hydrogens, which creates a significant amount of NH\textsubscript{3} and B\textsubscript{2}H\textsubscript{6} or even Al(BH\textsubscript{4})\textsubscript{3} upon the thermal decomposition. Anionic M[Al(NH\textsubscript{2})\textsubscript{3}]\textsubscript{n} and M[Al(BH\textsubscript{4})\textsubscript{3}] potentially might be combined in RHCs with other hydrides containing the counter-charged hydrogens. In particular, the interaction between M[Al(NH\textsubscript{2})\textsubscript{3}]\textsubscript{n} and M[Al(BH\textsubscript{4})\textsubscript{3}] is interesting, since the
ability of $\text{Al}^{3+}$ to coordinate both nitrogen or boron can be the good basis for the reversibility of the decomposition products. The family of $\text{M}[^{\text{Al(NH}_2\text{BH}_3})_4]$ is another interesting partly reversible system with high hydrogen content, with a potential for combining in RHCs with other hydrides.

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